

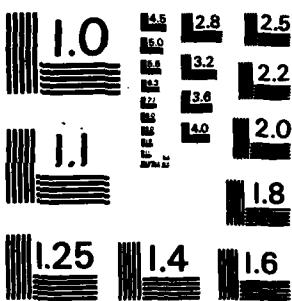
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Iridium Hydrides with Di(tertiaryphosphine) Bridges and Chelates
by
Richard Eisenberg and Barbara J. Fisher
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University of Rochester
Department of Chemistry
Rochester, New York 14627

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species $\text{IrH}_3(\text{CO})(\text{dppe})$. For dppp, all of the complexes are mononuclear with dppe acting as a chelate. The necessarily cis disposition of phosphine donors in the mononuclear chelates is readily evidenced by ¹H nmr spectroscopy of the hydride complexes.

The complex $\text{IrH}_3(\text{CO})(\text{dppe})$ is found to promote the carbonylation of benzene to benzaldehyde upon photolysis under CO. This arene C-H functionalization reaction appears to be thermodynamically limited. Long term photolyses show evidence of secondary products including benzylalcohol, as well as of complex decomposition.

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Iridium Hydrides with Di(tertiaryphosphine) Bridges and Chelates

Richard Eisenberg and Barbara J. Fisher
Department of Chemistry
University of Rochester
Rochester, New York

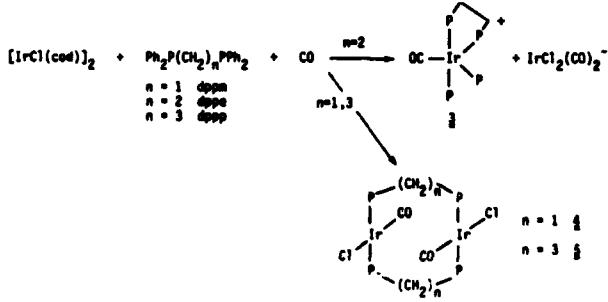
Introduction

→ The activation of substrate is an essential step in catalysis, and generally involves a weakening or breaking of bonds within the substrate. The effectiveness of transition metal complexes as catalysts is closely related to their ability to perform this process. Substrate activation is often accomplished by donation of electron density from filled metal d orbitals into vacant antibonding orbitals of the substrate, thus perturbing its electronic structure, and resulting in an oxidative addition reaction if a substrate bond is cleaved. Complexes of electron rich metals are particularly effective in activating substrates in this manner, and within this genre, no set of complexes has been more vigorously studied over the past two decades than those of Rh(I) and Ir(I). Complexes of these d⁸ ions possess a rich oxidative addition chemistry, and are active as catalysts for a variety of reactions including hydrogenations, hydroformylation, and carbonylations.¹

While complexes of Ir(I) are often not as catalytically active as analogous Rh(I) systems, the electron richness of Ir(I) frequently yields more stable substrate adducts and oxidative addition products.² In this context, Vaska's complex, IrCl(CO)(PPh₃)₂, is especially notable, undergoing reactions with numerous substrates including H₂, NX (X=Cl, Br, I), NaI, BaBr, RCOX, and R₃SiH among others.³ In this reaction chemistry and that of closely related analogs, the phosphine ligands L generally maintain their trans disposition and yield stable adducts having structures 1 or 2 depending on the substrate IV and the mechanism of adduct formation.

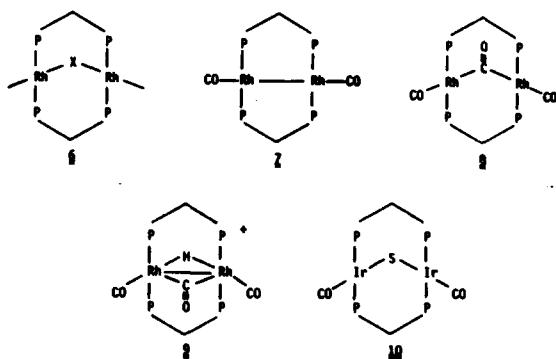
In this paper, we describe our studies on iridium complexes containing di(tertiary phosphine) ligands. These ligand systems may either chelate a single metal center or bridge two Ir ions. The former leads to a *cis* stereochemistry of phosphine donors different from that observed in most adducts of Vaska's complex and its analogs, while the latter produces two metal centers in close proximity for the binding and activation of substrates.

The relative tendency of the di(tertiary phosphine) ligand system $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ to bridge or chelate has been addressed by Sanger who synthesized a monomer only when $n=2$ and dimers when $n=1$ and 3 via eqn.(1).⁴ Compound **3**, which was first reported by Vaska, forms because of the favorable driving force of five-membered chelate ring formation.⁵ Complexes **4** and **5**, on the other hand, maintain what seems to be the electronically favorable disposition of trans P donors with the creation of face-to-face dimers of Ir(I) having ligand sets similar to that found in Vaska's complex.



Our interest in dimeric compounds of this type was stimulated by the notion of two metal centers in close, fixed proximity for the activation of the substrates simultaneously, or for the activation of a single substrate using both metal centers and their attendant $d\delta$'s (two $d\delta + d\delta$ oxidative

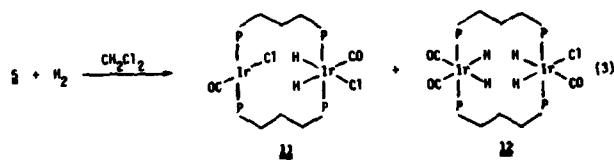
additions on a single substrate). To improve the orientation of the two $d\delta$ metal ions on **3**, we devised a series of molecules called molecular A-frames, **6**. In previous papers, we have described the chemistry of some of these dppe complexes including **7** - **10**.⁶



Complex **2** is modestly active as a catalyst for the water gas shift reaction, eqn.(2), but its catalyst lifetime is relatively short. Complex **10** forms reversible adducts with CO and with Hg but not with both simultaneously. Further studies on these and related A-frame systems are in progress.⁷

While the dppe **10** ligand keeps the two bridged metal centers in close proximity, the dppp ligand allows the binuclear complexes to be more flexible with metal...metal distances ranging from ~3.5 Å to 36 Å. The chemistry of **5** has recently been explored by Pignolet and Wang who find that **5** oxidatively adds Hg to form a mixture of the dihydride $[\text{Ir}_2\text{Hg}(\text{CO})_2\text{Cl}_2(\text{dppp})_2]$, **11**, and the

tetrahydride $[\text{Ir}_2\text{H}_2(\text{CO})_2\text{Cl}_2(\text{dppp})_2]$, **12** in eqn. (3).⁸



The structural assignments of **11** and **12** are supported by crystallographic evidence. Loss of H_2 from **12** appears facile, and the increased steric bulk at one Ir center after the first oxidative addition appears to inhibit reactivity at the second metal center.

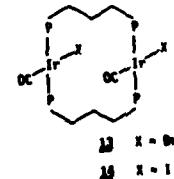
The studies described in this paper use the work of Sanger and Pignolet as a starting point. Because the bromo and iodobromo analogs of Vaska's complex were known to be more reactive than the parent chloro system $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, we commenced studies on the bromo and iodo analogs of **3**. The context in which our studies were undertaken was the development of H_2 reduction catalysts for CO_2 , a goal that still remains to be reached. Based on Herkowitz' work, it was known that electron rich $\text{Ir}^{(I)}$ centers are capable of reacting with CO_2 .⁹ We envisioned that the presence of nearby hydrides on a second metal center would facilitate the desired reduction of bound CO_2 .

The investigations which we outline here include studies of bimetallic dppp complexes and the hydrides which they form, the cleavage of these dimers into mononuclear species, and the formation and reaction chemistry of previously unknown mononuclear complexes containing only one dppp ligand. One of these dppp systems upon irradiation activates aromatic C-H bonds and promotes the formation of benzaldehyde and benzyl alcohol from benzene and synthesis gas. This reaction represents an important example of C-H bond functionalization.

The Synthesis and Characterization of New Iridium Hydrides Containing D(tertiary phosphine) Ligands

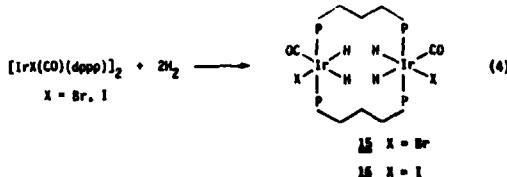
The iridium(I) anion $[\text{Ir}(\text{CO})_2\text{Br}_2]^-$ as its $n\text{-BuLi}$ salt serves as the convenient starting material for the preparation of the mono- and bimetallic complexes of iridium reported here.

dppp Complexes. The room temperature reaction of $(n\text{-BuLi})[\text{Ir}(\text{CO})_2\text{Br}_2]$ with dppp in acetone under H_2 leads to the evolution of CO and the essentially quantitative production of the pale yellow complex $[\text{Ir}\text{Br}_2(\text{CO})_2(\text{dppp})_2]$, **13**. The dimeric structure of **13** is assigned based on elemental analyses, a singlet



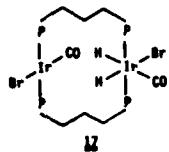
at δ 19.03 in the ^{31}P nmr spectrum of the complex, and by analogy with the chloro complex **3** reported by Sanger. The CO ligands in **13** are shown in a cis orientation because of two vpp's at 1944 and 1915 cm^{-1} . The diido complex **14** is prepared by metathesis using a 100 fold excess of **13** and a slurry of the chloro complex **3** in benzene and based on the single vpp at 1950 cm^{-1} , is assigned a structure with CO ligands in the trans orientation as found in **3**.

The oxidative addition of H_2 to **13** and **14** yields bimetallic hydride complexes. Under 1 atm H_2 in CH_2Cl_2 , **13** and **14** form the tetrahydride complexes **15** and **16**. The formation of **15** in THF at 25°C is essentially complete within 1 hr compared with 24 hr for the formation of **15** and only incomplete conversion of the chloro complex **3** to its tetrahydride **12** under the



same conditions. This observation is consistent with the notion of increased reactivity with halide ligand in the order $\text{Cl} < \text{Br} < \text{I}$. Oxidative addition of only a single molecule of H_2 to $\underline{\underline{13}}$ to yield the $\text{Ir}(\text{I})\text{-Ir}(\text{III})$ dihydride $\underline{\underline{12}}$ can be accomplished by using only one equivalent of H_2 . In acetone, the reaction of $\underline{\underline{13}}$ with H_2 yields a mixture of $\underline{\underline{15}}$ and $\underline{\underline{16}}$ because of the inhomogeneous nature of the reaction.

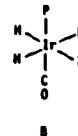
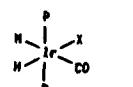
The binuclear hydrides $\underline{\underline{15}} - \underline{\underline{17}}$ were characterized spectroscopically, and relevant data are presented in Table I. The hydride region of the ^1H nmr



spectrum, as illustrated in Figure 1, is particularly informative, showing for each species two triplets of doublets separated by ~ 9 ppm indicating chemically different hydride ligands. The triplet splitting at each chemical shift is 13 Hz, and is due to coupling to two equivalent P nuclei. The doublet splitting is 3 Hz and is due to Δg_{Ir} between the two hydrides. Mononuclear decoupling of each triplet results in the loss of doublet splitting at the other. These observations are consistent with "micro" structure $\underline{\underline{A}}$ in which the phosphine donors are trans.

Additional support for our interpretation of the ^1H nmr spectral data is obtained by analogy to the known mononuclear hydride complexes $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_2]$ which possess geometry $\underline{\underline{A}}$. The ^1H nmr spectra of these complexes is essentially the same as we observe for $\underline{\underline{15}} - \underline{\underline{17}}$.

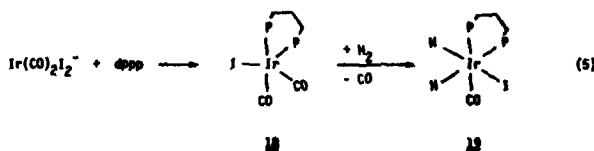
A very different hydride pattern is obtained, however, when a reaction solution of $\text{Ir}(\text{CO})_{2}\text{ig}^+$ + dppp is treated with H_2 . Prior to treatment with H_2 , a complex may be isolated which exhibits ν_{CO} at 2040 and 1955 cm^{-1} and a singlet in the ^3P nmr spectrum at $\delta = 20.5$. The ^1H nmr spectrum obtained upon the addition of H_2 is shown in Fig. 2. The main features of the hydride pattern are two groups of resonances separated by ~ 6 ppm, one of which is a broad doublet of doublets and the other a more complicated multiplet. The spectrum is consistent with chemically different P nuclei, and the magnitude of the larger doublet-of-doublets splitting ($\Delta \nu_{\text{H}} = 120$ Hz) suggests that one of the hydrides is trans to a phosphine donor. "Micro" structure $\underline{\underline{B}}$ is consistent with the ^1H nmr results. The second hydride is located trans to CO ligand based on its chemical shift.



The spectroscopic data provide the basis for a consistent interpretation of the reactions involving $\text{Ir}(\text{CO})_{2}\text{ig}^+$ + dppp and H_2 as shown in eqn.(5). The initial product having ν_{CO} of 2040 and 1955 cm^{-1} is mononuclear, unlike the other dppp complexes formed in analogous reactions, and the two carbonyl stretches indicate a cis disposition of CO ligands in the complex. This complex, $[\text{Ir}(\text{CO})_2(\text{dppp})]$, is assigned structure $\underline{\underline{18}}$ with a chelating di(tertiary

-8-

phosphine) ligand. The singlet in the 31P nmr spectrum of **12** may be ascribed to stereochemical nonrigidity of this five coordinate d5 species. The reaction of **12** with H₂ leads to loss of CO, which is detected in the gas phase



above the solution, and the formation of **12** which possesses "micro" structure **A**. Alternative binuclear formulations of **12** and **13** with bridging dppp ligands in cis positions of the coordination sphere are ruled out based on highly unfavorable steric interactions between neighboring diphenylphosphine groups, and parallel reaction chemistry observed using dpp which is discussed below.

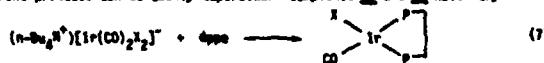
Cleaving dppp-Bridged Binuclear Hydrides. When CH₂Cl₂ solutions of the binuclear hydride complex **12** is refluxed for extended times or heated in the presence of NEt₃ for shorter times (2-5 hrs), a striking change occurs in the hydride region of the 1H nmr spectrum. Specifically, the resonances characteristic of arrangement **A** are replaced by those consistent with arrangement **B**. The change from trans to cis P donors occurs with a cleavage of the binuclear hydride system to the mononuclear structure **20** as shown in eqn.(6).



-9-

The lack of integrity of **12** as a binuclear species was surprising since Pignolet and Wang had employed harsher conditions in their hydrogenation experiments with [IrCl(CO)(dppp)]₂, **5**, and had not observed any evidence of dimer cleavage. Moreover, reactions of similar complexes having dppp bridges under a variety of conditions have revealed no tendency of these dimers to break apart into monomeric species. Our observation of dimer cleavage provides an important caveat to studies based on using di- and poly(tertiary phosphine) ligands to hold two or more metal atoms together in systems having structural integrity.

dppe Complexes. In order to provide additional support for the structure assignments of **12-20** as mononuclear species, the analogous complexes with dppe in place of dppp were synthesized and characterized. The ligand dppe shows a much greater tendency towards cleavage than does dppp, and only rarely forms a bridge between two metals. The new mononuclear mono(dppe) complexes **Ir(CO)X(dppe)**, **21(X=Br)** and **22(X=I)**, were prepared by reacting (n-Bu₄N)⁺[Ir(CO)₂I₂] with dppe in refluxing THF or benzene according to eqn.(7). Formation of **21** in this reaction cannot be avoided but the two different products can be easily separated. Complexes **21** and **22** have very



21 X = Br

22 X = I

similar spectroscopic properties (see Table I). The single vpp of 1900 cm⁻¹ for **21** and 1900 cm⁻¹ for **22** and the two doublets in the 31P nmr spectrum of each complex provide convincing evidence that **21** and **22** are mononuclear mono(dppe) species.

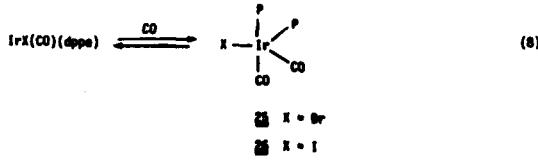
Solutions of the orange, square planar Ir(I) complexes **21** and **22** in THF or CH₂Cl₂ react extremely rapidly with H₂ to form the mononuclear dihydride

species 23 and 24, respectively. These complexes are readily isolated as



colorless crystals by the addition of EtOH and removal of solvent. Complexes **23** and **24** are spectroscopically similar to complexes **19** and **20** (see Table I). The hydride region of the ^1H nmr spectrum of **23** is shown in Figure 3. The "downfield" hydride resonance is a doublet of doublets of doublets ($\delta_{\text{H-P}} = 130$ Hz; $\delta_{\text{H-P}} = 17$ Hz; $\delta_{\text{H-P}} = 4.5$ Hz), and is separated from the "upfield" hydride multiplet by 9 ppm. Irradiation of the upfield multiplet results in loss of the smallest doublet splitting in the downfield hydride resonances, leaving a doublet of doublets pattern. The observation of hydride-hydride coupling for **23** and **24** represents the only difference in their ^1H nmr spectra from those observed for the analogous dppp complexes, **19** and **20**.

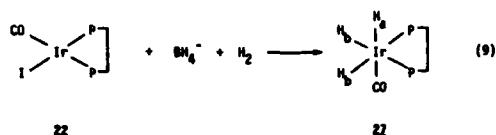
The addition of H_2 to 21 and 22 is reversible, as is the addition of CO to form the five-coordinate dicarbonyl complexes 25 and 26 which are analogous to 18 , eqn.(8). Refluxing THF or benzene solutions of these adducts under H_2



leads to loss of the addend molecule and regeneration of 21 or 22 . The dicarbonyl complexes 25 and 26 exhibit two νCO 's at 1940 and 2040 cm^{-1} , and at

1950 and 2040 cm^{-1} , respectively, in close parallel with 18.

Preparation and Characterization of $\text{IrH}_3(\text{CO})(\text{dppc})$. The trihydride complex $\text{IrH}_3(\text{CO})(\text{dppc})$, 22, is a particularly interesting compound which was prepared according to eqn. (9) by the reaction of NaBH_4 in ethanol with 22 in CH_2Cl_2 under H_2 . This complex was isolated as a tan, air stable powder, and when



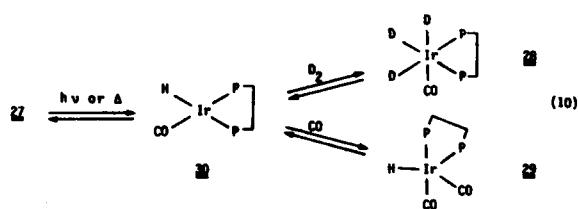
recrystallized, is colorless. The hydride region of the ^{1}H NMR spectrum of 22 is shown in Figure 4 and based on the splitting pattern observed, a facial configuration for the hydrides can be assigned unambiguously. The apical hydride, H_α , is unique, and is cis to the 2 P donor atoms of dppc, giving rise to the triplet at $\delta = -10.86$ ppm ($J_{\text{P},\text{H}} = 19$ Hz). The equatorial hydrides, H_β , are chemically equivalent, ($\delta = -9.27$ ppm) and are split by a trans P ($J_{\text{P},\text{H}} = 124$ Hz), a cis P ($J_{\text{P},\text{H}} = -12.2$ Hz) and each other (4.5 Hz). A computer simulation of the hydride region confirms these assignments and is shown in Figure 4.

We found that complex **22** loses H₂ both thermally and photochemically, with the rate of photogenerated loss much greater. This was demonstrated by photolyzing **11** in benzene-d₆ solution under O₂ and CO, and monitoring the ¹H nmr spectral changes with time. In reactions under O₂ and CO, only the hydride region of the spectrum was affected. After short photolysis times (20 m) or longer thermolysis times (2 h), the outermost doublets of the -9.27 ppm resonance were observed to lose their hydride-hydride coupling as shown in Figure 4, and the integrated intensity of the hydride resonances decreased by

~ 50% relative to the dppc resonances of the complex. After 2.5 h of photolysis, only traces of the hydride resonances remained, indicating that deuterium incorporation was essentially complete, converting $\underline{27}$ to $\text{IrD}_3(\text{CO})(\text{dppc})$, $\underline{28}$. This conversion requires 8 h thermally. The IR spectrum of the isolated product (see Table) together with the ^1H nmr data support the formulation of complex $\underline{28}$ as $\text{IrD}_3(\text{CO})(\text{dppc})$. When $\underline{28}$ dissolved in CgB_6 is photolyzed under H_2 , it is converted back to the trihydride, $\underline{27}$.

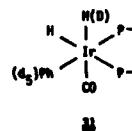
Photolysis or thermolysis of $\underline{27}$ in benzene under CO leads to the rapid appearance of a new hydride resonance at $\delta = 10.36$ ppm (τ) accompanied by new resonances in the methylene and phenyl regions of the spectrum. After 2.5 h of irradiation, all resonances of $\underline{27}$ are replaced by ones associated with the new triplet at -10.36 ppm. (The thermal reaction is complete in 8 h.) The phenyl and methylene regions in the ^1H nmr spectrum of this material are nearly identical to those of the five coordinate $\text{Ir}(\text{I})$ complex $\text{IrH}(\text{CO})_2(\text{dppc})$, $\underline{29}$, which forms by CO addition to $\underline{27}$. A larger scale photolysis of $\underline{27}$ under CO allows isolation of this new material which we identify as $\text{IrH}(\text{CO})_2(\text{dppc})$, $\underline{29}$, based on nmr and IR spectral data. Both $\underline{28}$ and $\underline{29}$ exhibit only sharp singlets in their $^{31}\text{P}(\text{H})$ nmr spectra indicating equivalence of the two dppc donors in each complex at room temperature. Complex $\underline{29}$ may also be prepared from $\underline{27}$ and BH_4^- under a CO atmosphere in absolutely dry solvents.

The formation of $\underline{28}$ and $\underline{29}$ by photolysis or thermolysis of the trihydride $\underline{27}$ under D_2 and CO, respectively, is consistent with the reductive elimination of H_2 from $\underline{27}$, generating the reactive 4-coordinate species $\text{IrH}(\text{CO})(\text{dppc})$, $\underline{30}$, which then adds D_2 or CO as shown in eqn.(10). The formation of the trideuteride $\underline{28}$ requires at least two passes through the reductive elimination/oxidative addition sequence in eqn.(10) with production of one equivalent of HD . The photochemically promoted reductive elimination of H_2 from metal polyhydrides is now well documented, and has been found in a number of cases to generate highly reactive species.¹⁰



The proposed four-coordinate $\text{Ir}(\text{I})$ intermediate, $\underline{30}$, is reactive to other substrates including benzene. When a benzene- d_6 solution of $\underline{27}$ is photolyzed under D_2 or vacuum, a change in the hydride spectrum similar to that seen under D_2 as shown in Fig. 4 is observed after 20 m, along with a corresponding loss in the integrated intensity of the hydride resonances relative to those of dppc. This result indicates that deuterium incorporation into $\underline{27}$ is taking place with the solvent serving as the deuterium source.

Although a phenyl hydride species $\underline{31}$ corresponding to the oxidative addition product of benzene to $\text{IrH}(\text{CO})(\text{dppc})$ is not seen directly, the observed H/D exchange is most readily explained by its intermediacy.



Carbylation of Benzene to Benzaldehyde. The proposed existence of $\underline{31}$ stimulated further experiments to determine if CO insertion and elimination of carbylated product could be seen. This was indeed the case. In all photolyses of $\underline{27}$ in CgB_6 under CO or CO/ H_2 mixture, a new resonance in the ^1H

nmr spectrum at δ 9.63 ppm was observed which is assignable to benzaldehyde. The only other observed change in the ^{13}C nmr spectrum was complete conversion of $\underline{\text{Z}}$ to $\underline{\text{M}}$ as noted above. Experiments were done to confirm the formation of benzaldehyde. Photolysis of $\underline{\text{Z}}$ in C_6D_6 under 600 torr CO followed by gc analysis of the volatiles showed benzaldehyde present. Treatment of the volatiles with semicarbazide yielded a white crystalline material which was shown to be benzaldehyde semicarbazone. In all cases, the amounts of benzaldehyde detected by gc analysis were small (5-8 mM after 8 h of photolysis). The carbonylation reaction does not appear to go thermally. When $\underline{\text{Z}}$ in C_6D_6 under 600 torr CO is heated at 90°C for 5 days no evidence of benzaldehyde formation is found by either gc or nmr methods.

The formation of benzaldehyde when $\underline{\text{Z}}$ is photolyzed in benzene under CO indicates the occurrence of eqn.(11), and represents an important example of C-H functionalization. The small amounts of benzaldehyde formed may be the



result of unfavorable thermodynamics for eqn.(11). We calculate ΔG° and K_{eq} at 290°C for eqn.(11) as +1.7 kcal/mole and 5.9×10^{-2} atm $^{-1}$, respectively. It should be noted that uncertainties in entropy values for liquid benzene and benzaldehyde permit a range of ΔG and K values to be calculated, but in all cases the reaction is thermodynamically unfavorable. This notion is confirmed when the trihydride $\underline{\text{Z}}$ is photolyzed in C_6D_6 in the presence of $\text{C}_6\text{D}_5\text{OD}$ under vacuum. Within 5 min, the formation of the dicarbonyl species $\underline{\text{M}}$ was noted, and after 8 hrs, the conversion of $\underline{\text{Z}}$ to $\underline{\text{M}}$ was complete and the benzaldehyde had decreased to a small but relatively steady value with a concomitant increase in the benzene resonance. It thus appeared that the equilibrium of eqn.(11) was being approached from either direction.

Attempts were then made to determine K_{eq} and ΔG of (11) experimentally.

However, gc analysis of solutions from prolonged irradiation (>36 hours) revealed a new product which has been identified by gc and nmr techniques to be benzyl alcohol. This result may prove to be highly significant since the reduction of benzaldehyde to benzyl alcohol, eqn.(12), is thermodynamically favorable (ΔG is between -5 and -8 kcal/mole depending on the entropy values used).



The reaction may thus serve as a convenient drain for equilibrium (11) so that benzene carbonylation can proceed productively. Longer term photolyses of $\underline{\text{Z}}$ in C_6D_6 under 1:1 CO:Hg (600 torr), however, reveal only the formation of ~ 2 equivalents of benzyl alcohol. While the only Ir complex detectable appears to be $\underline{\text{M}}$, which can reenter the catalytic cycle by dissociation of CO, additional products are formed in these longer term experiments (125 hrs) as evidenced by the development of yellow and orange colors in the reaction solution.

Further studies to examine the trihydride, $\underline{\text{Z}}$, and the dicarbonyl hydride, $\underline{\text{M}}$, as catalysts for arene C-H bond functionalization are continuing.

Summary

In this paper we have examined the synthesis and characterization of tridium hydrides having di(tertiary phosphine) ligands as bridges and chelates. Binuclear dppp bridges complexes of formula $[\text{IrH}_2(\text{CO})(\text{dppp})]_2$ where X = Br, I possess the phosphine donors in trans disposition as shown by ^{31}P nmr spectroscopy. Upon heating, these dimers cleave into monomeric species of the same stoichiometry. The dppp complexes are all unimolecular and contain a chelated di(tertiary phosphine) ligand. The hitherto unreported $[\text{Ir}(\text{CO})(\text{dpp})X]_2$ complexes have been described as has their reaction

chemistry to form reversible adducts with CO and H₂. The trihydride complex IrH₃(CO)(dppe) in C₆H₆ under CO leads to the formation of benzaldehyde in possibly thermodynamically-limited amounts. An intriguing observation under continuing study is the subsequent conversion of benzaldehyde to benzyl alcohol. These observations represent an important example of C-H bond functionalization.

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Table I. Spectroscopic Data of Iridium dppp and dppe Complexes

Compound	IR(cm ⁻¹) ^a	31P NMR	1H NMR (Hydride region only)
[Ir ₂ Br ₂ (CO) ₂ (dppp) ₂] ¹³	1915, 1944	19.03(s) ^c	
[Ir ₂ I ₂ (CO) ₂ (dppp) ₂] ¹⁴	1950	14.0(s) ^c	
[Ir ₂ H ₄ Br ₂ (CO) ₂ (dppp) ₂] ¹⁵	1945, 1980	2100, 2190 0.04(s), 7.47(s) ^c	-8.6 (t of d), -18.7 (t of d) J _{PH-cis} = 13 Hz, J _{HH} = 3 Hz (CDCl ₃)
[Ir ₂ H ₄ I ₂ (CO) ₂ (dppp) ₂] ¹⁶	1980	2090, 2160	-9.74 (t of d), -16.84 (t of d) J _{PH-cis} = 13 Hz, J _{HH} = 3 Hz (CDCl ₃)
[Ir ₂ H ₂ Br ₂ (CO) ₂ (dppp) ₂] ¹⁷	1945, 1980	2100, 2190	-8.4, -8.8, -18.2, -18.6 (all t of d) J _{PH-cis} = 13 Hz, J _{HH} = 3 Hz (CDCl ₃)
IrI(CO) ₂ (dppp) ¹⁸	1955, 2040	-28.49(s) ^c	
IrH ₂ I(CO)(dppe) ¹⁹	2042	2105 J _{p-p} =30.52 Hz	-5.27 (d of d, J _{PH-trans} = 120 Hz, J _{PH-cis} = 16 Hz), -15.35 (m) (C ₆ D ₆)
IrH ₂ Br(CO)(dppp) ²⁰	2043	2220	-9.27 (d of d, J _{PH-trans} = 120 Hz, J _{PH-cis} = 16 Hz), -17.99 (m) (C ₆ D ₆)
IrBr(CO)(dppe) ²¹	1980	43.7(d), 47.9(d) ^d J _{p-p} =14 Hz	
IrI(CO)(dppe) ²²	1980	64.3(d), 62.21(d) ^d J _{p-p} =9.5 Hz	
IrH ₂ Br(CO)(dppe) ²³	2030	2195 33.8(d), 26.6(d) ^d	-9.05 (d of d of d, J _{PH-cis} = 17 Hz, J _{PH-trans} = 130 Hz, J _{HH} = 4.5 Hz), -18.26 (m) (CDCl ₃)
IrH ₂ I(CO)(dppe) ²⁴	2040	2160 J _{p-p} =7 Hz	-9.92 (d of d of d, J _{PH-cis} = 17 Hz, J _{PH-trans} = 128 Hz, J _{HH} = 4.5 Hz, -16.27 (m) (acetone-d ₆)
IrBr(CO) ₂ (dppe) ²⁵	1940, 2040	53.51(s) ^d	
IrI(CO) ₂ (dppe) ²⁶	1950, 2040	32.0(s) ^d	
IrH ₃ (CO) ₂ (dppe) ²⁷	2010	1940, 2000, 2060 30.8(s) ^d	-9.48 (d of d of d, J _{PH-trans} = 124 Hz, J _{PH-cis} = -12.2 Hz, J _{HH} = 4.5 Hz), -10.86 (t, J _{PH-cis} = 19 Hz) (C ₆ D ₆)
IrP ₃ (CO)(dppe) ²⁸	2030	b	
IrH(CO) ₂ (dppe) ²⁹	1913, 1966	2000 33.8(s) ^d	-10.36 (t, J _{PH-cis} = 41 Hz) (C ₆ D ₆)

Table I (continued)

- a. IR Spectra were recorded on a Perkin-Elmer 467 Grating Infrared Spectrophotometer. All spectra were taken of KB pellets except for 18, 25 and 26 which were in benzene solution.
- b. v_{IR}-D not observed
- c. All proton nmr spectra recorded on a Bruker WH-400 at 400.134 MHz. Positive chemical shifts are downfield from TMS.
- d. Measured in 5 mm tubes on Bruker WH-400 at 162 MHz. Positive chemical shifts are downfield from Hg^{2+} (external).
- e. Measured in 10 mm tubes on Jeol PFT-100 spectrometer at 41.25 MHz.

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Figure Captions

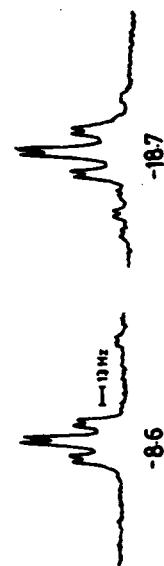
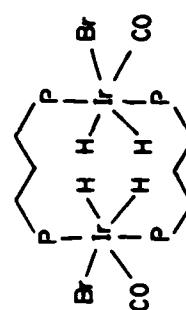
Figure 1. Hydride Region of **15**

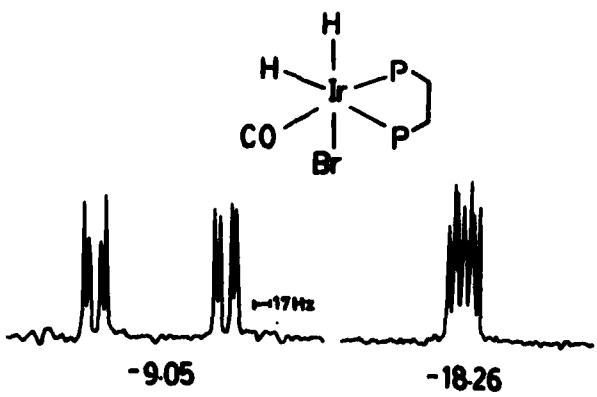
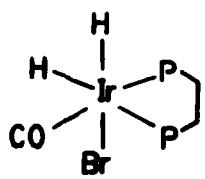
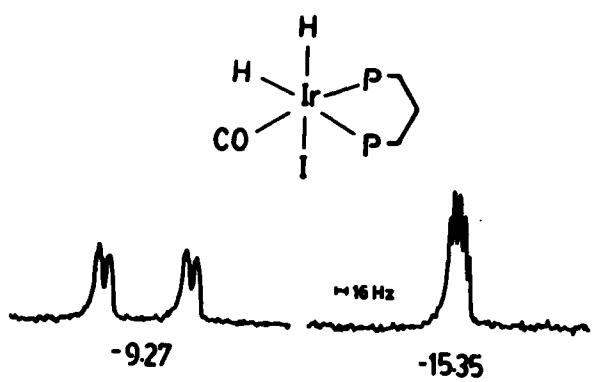
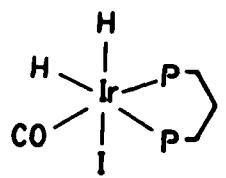
Figure 2. Hydride Region of **19**

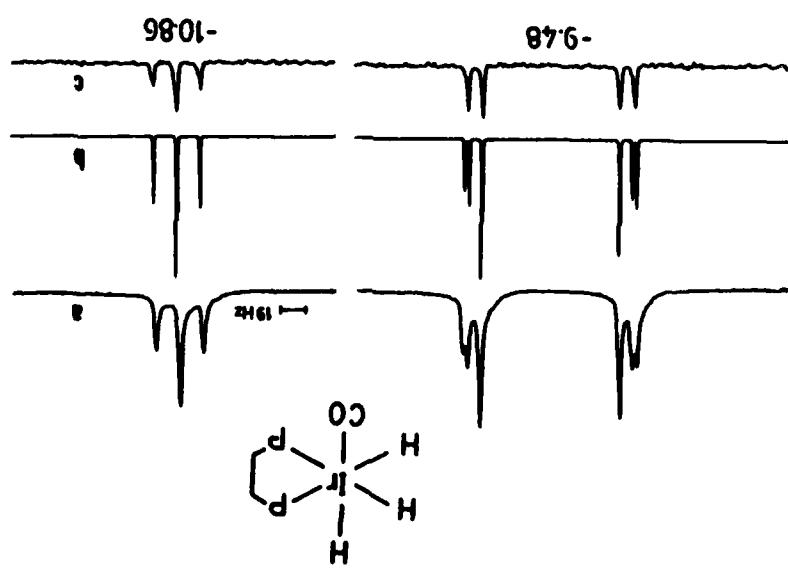
Figure 3. Hydride Region of **23**

Figure 4. Hydride Region of **27**. a. Experimental spectrum. b. Simulated spectrum

c. Partial deuteration after thermolysis of **27** under D₂ for 8 h.







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